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(54) Title: UNIVERSAL WELL CEMENT ADDITIVES AND METHODS

(57) Abstract

The present invention provides universal well cement additives and methods. The universal well cement additives improve the properties of a well cement slurry and can be comprised of iron chloride, a dispersing agent, an organic acid, a hydratable polymer and an ultra–fine particulate hydraulic cement.

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UNIVERSAL WELL CEMENT ADDITIVES AND METHODS

Related Patent Application Data

This application is a continuation-in-part of application Serial No. 09/013,791 filed January 26, 1998 which is a continuation-in-part of application Serial No. 08/834,065 filed April 14, 1997, now Patent No. 5,749,418 issued May 12, 1998.

Background of the Invention

1. Field of the Invention.

The present invention relates generally to well cement additives, and more particularly, to universal composite additives for improving the properties of well cement slurries.

2. Description of the Prior Art.

Hydraulic cement slurries used for cementing subterranean formations or zones in oil and gas wells must have particular properties. For example, the slurries must have properties such that they are capable of being mixed and pumped without prematurely gelling, have sufficiently long pumping times to be placed in subterranean formations or zones, have sufficiently high compressive strengths after setting, and have good fluid loss control.

The American Petroleum Institute (API) has set standards for different classes of oil well cements to insure that the cement slurries formed with them have required properties. The API cements are Portland cements and because of the strict requirements placed on them, they are more difficult to produce and more expensive than the many construction grade cements used for constructing bridges, roads, buildings and the like on the earth's surface.

Surface construction grade cements are commonly available from a variety of manufacturers throughout the world and are very inexpensive as compared to API Portland cements and other comparable cements used in cementing oil and gas wells. The construction grade cements typically contain high quantities of metal sulfates while the cements used in oil well cementing must have relatively low metal sulfate contents.

While cement slurries formed from inexpensive surface construction grade cements are suitable for a large number of surface applications, they do not have the properties required for subterranean oil and gas well cementing such as consistent viscosities, suitable thickening times, high compressive strengths after setting, good fluid loss control and the like. The chemical compositions, and particularly the metal sulfate concentrations, of surface construction grade cements vary from manufacturer to manufacturer making it impossible to predict the properties of cement slurries containing such cements. Thus, there is a need for a universal additive for improving the properties of inexpensive surface construction grade cement slurries whereby the slurries can be used in oil and gas well cementing applications.

A number of low quality oil and gas well cements which are available and used throughout the world also contain high metal sulfate concentrations and/or otherwise lack some of the properties required. For example, such low quality oil and gas well cements often have poor rheology, marginal strength development or poor response to conventional additives. Thus,

there is also a need for a universal additive that can be utilized to improve the properties of presently used low quality oil and gas well cements.

Summary of the Invention

The present invention provides universal composite particulate solid additives for improving the properties of well cement slurries which meet the needs described above and overcome the deficiencies of the prior art. When added to a surface construction grade or presently used oil and gas well grade hydraulic cement slurry, an additive of this invention simultaneously improves the viscosity, thickening time, after setting compressive strength, fluid loss control and other properties of the slurry to those which are particularly suitable for cementing oil and gas wells.

The universal additives of this invention are comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight, a dispersing agent present in an amount in the range of from about 1 to about 20 parts by weight, an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight, a hydratable polymer present in an amount in the range of from about 1 to about 20 parts by weight and an ultra-fine particulate hydraulic cement present in an amount in the range of from about 1 to about 50 parts by weight. Other components which can optionally be included in the additive are a defoaming agent, an alkaline earth metal halide and one or more

other agents for increasing the set cement compressive strength.

Additional universal additives of this invention are comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight, an alkali or alkaline-earth metal halide, preferably chloride, present in an amount in the range of from about 5 to about 60 parts by weight, an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight and a hydratable polymer present in an amount in the range of from about 1 to about 50 parts by weight. Other components which are also preferably included in the additive are a defoaming agent, a dispersing agent, ultra-fine particle size hydraulic cement and other agents for increasing the set cement compressive strength.

The methods of this invention for improving the properties of a cement slurry comprised of a surface construction grade or better hydraulic cement and water comprise combining a universal additive of the present invention with the cement slurry in an amount in the range of from about 0.1% to about 30% by weight of the hydraulic cement in the slurry, the universal additive being comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof, a dispersing agent, an organic acid, a hydratable polymer and an ultra-fine particulate cement.

Additional methods of this invention for improving the

properties of a cement slurry comprised of a surface construction grade or better hydraulic cement and water comprise combining a universal additive of the present invention with the cement slurry in an amount in the range of from about 0.1% to about 30% by weight of the hydraulic cement in the slurry, the universal additive being comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof, an alkali or alkaline-earth metal halide, an organic acid, and a hydratable polymer.

Methods of cementing a subterranean zone penetrated by a well bore utilizing a cement slurry comprised of a surface construction grade or better hydraulic cement and water are also provided by the present invention. The methods comprise the steps of combining a universal additive of this invention as described above with the cement slurry in an amount in the range of from about 0.1% to about 30% by weight of the hydraulic cement in the slurry, pumping the cement slurry containing the additive into the subterranean zone to be cemented by way of the well bore and then allowing the cement slurry to set into a hard impermeable mass therein.

It is, therefore, a general object of the present invention to provide universal well cement additives and methods of using the additives.

Other and further objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments which follows.

Description of Preferred Embodiments

As mentioned above, construction grade cements for use in surface applications and low quality oil and gas well cements are readily available from a variety of manufacturers around the world and are very inexpensive as compared to the high quality API cements often used in cementing oil and gas wells. The surface construction grade and low quality oil and gas well cements typically contain high quantities of alkali and/or alkaline-earth metal sulfates, i.e., from about 0.75% to about 3.0% of such metal sulfates by weight of the cement. High quality API oil and gas well cements typically contain less than about 0.3% of such metal sulfates by weight of the cement. The presence of the high amounts of metal sulfates in the cements causes the cements to have varying and erratic properties such as thickening time and compressive strength when slurried in water.

The present invention provides single universally applicable particulate solid additives which contain mixtures of components that react synergistically with cement slurries to optimize the properties of the cement slurries and their performance in cementing oil and gas wells. The additives are not only useful in improving the properties and performance of surface construction grade and low quality oil and gas well cement slurries, but they also improve the properties and performance of other well cements including those meeting API standards. The additives are particularly useful in improving the properties of cements available in remote locations

throughout the world whereby the cements can be effectively utilized in oil and gas well cementing.

The four basic properties of a cement slurry which the additives of the present invention improve to make the cement slurry suitable for oil and gas well cementing are viscosity (also referred to as rheology), thickening time, after setting compressive strength and fluid loss control. As mentioned, the additives of this invention are universally applicable to cement slurries formed with low quality high sulfate content cements as well as those formed with higher quality cements. The additives can be used to improve the properties of cement slurries which are to be subjected to temperatures up to about 230°F and which have densities in the range of from about 12 to about 17 pounds per gallon.

The universal additives of this invention are basically comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight, a dispersing agent present in an amount in the range of from about 1 to about 20 parts by weight, an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight, a viscosity increasing hydratable polymer present in an amount in the range of from about 1 to about 20 parts by weight and an ultra-fine particulate hydraulic cement present in an amount in the range of from about 1 to about 50 parts by weight.

As indicated above, the iron chloride can be ferrous

chloride, ferric chloride or mixtures thereof. The iron chloride functions synergistically with the other components of the additive to overcome the effect of a high metal sulfate concentration in a cement and to shorten the thickening time of a slurry of the cement to an acceptable range. That is, the iron chloride in combination with the other components of the additive causes the cement to hydrate in a normal and predictable manner. Also, the iron chloride contributes to improving the compressive strength of the cement slurry after it sets.

The dispersing agent in the additive helps control the rheology of the cement slurry and contributes to making the slurry a stable suspension over a broad density range. While various dispersing agents can be utilized, a particularly suitable dispersing agent is the condensation polymer product of an aliphatic ketone, e.g., acetone, an aliphatic aldehyde, e.g., formaldehyde, and a compound which introduces acid groups into the polymer, e.g., sodium sulfite. Such a dispersing agent is described in U.S. Patent No. 4,557,763 issued to George et al. on December 10, 1985, which is incorporated herein by reference, and is commercially available under the trade designation "CFR-3™" from Halliburton Energy Services of Duncan, Oklahoma.

The organic acid in the additive controls the viscosity of the cement slurry, i.e., it prevents the premature gelation of the slurry and improves the rheology of the slurry over a broad density range. Various organic acids can be utilized in the

additive including, but not limited to, tartaric acid, citric acid, gluconic acid, oleic acid, phosphoric acid and uric acid. Of these, tartaric acid is preferred.

A variety of viscosity increasing hydratable polymers can also be utilized in the additive including, but not limited to, carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers and other hydratable polymers known to those skilled in the art. Of these, hydroxyethylcellulose is preferred. The hydratable polymer utilized adds viscosity to the cement slurry and functions to reduce fluid loss from the slurry.

The ultra-fine particulate hydraulic cement in the additive preferably has a maximum particle size of about 15 microns and a specific surface area of about 12,000 square centimeters per gram. The distribution of the various size particles within the ultra-fine cement is preferably such that about 90% of the particles have diameters no greater than about 10 microns, 50% have diameters no greater than about 5 microns, and 20% of the particles have diameters no greater than about 3 microns. The specific surface area of the ultra-fine hydraulic cement (sometimes also referred to as Blaine fineness) is an indication of the ability of the cement to chemically interact with other materials. The specific surface area is preferably greater than about 12,000 square centimeters per gram, and more preferably, greater than about 13,000 square centimeters per gram.

Ultra-fine cements having maximum particle sizes and surface areas as set out above are disclosed in various prior U.S. patents including U.S. Patent No. 4,761,183 issued to Clarke during August 1988 which discloses ultra-fine particle size cements formed of slag and mixtures thereof with Portland cement and U.S. Patent No. 4,160,674 issued to Sawyer during July 1979 which discloses ultra-fine particle size Portland cements, both of which are incorporated herein by reference. The ultra-fine hydraulic cement preferred for use in accordance with this invention is Portland cement. Such a cement is commercially available under the trade designation "MICRO-MATRIX™" from Capitol Cement Co. of San Antonio, Texas. The presence of the ultra-fine cement in the cement slurry adds compressive strength to the cement slurry after it sets and contributes to shortening the thickening time of the cement slurry to a preferred range.

As indicated above, the additive can also include a number of other components which provide improved properties to a cement slurry. That is, the additive can include a defoaming agent such as polydimethylsiloxane present in the additive in an amount in the range of from about 0.01 to about 5 parts by weight. Such a defoaming agent is commercially available under the trade name "D-AIR™" from Halliburton Energy Services of Duncan, Oklahoma. The defoaming agent prevents a cement slurry containing the additive from excessively foaming during mixing and pumping.

Another component which can be included in the additive is

an alkali or alkaline-earth metal halide which functions with the iron chloride to overcome the effect of high metal sulfate concentration. Preferred such compounds are calcium chloride, sodium chloride, potassium chloride and ammonium chloride, with calcium chloride being the most preferred. When used, the alkali or alkaline earth metal halide is generally included in the additive in an amount in the range of from about 5 to about 20 parts by weight.

Still another component which can be included in the additive is a particulate ASTM Type III cement which contributes to increasing the after setting compressive strength of the cement slurry and decreasing the thickening time of the slurry. Such a cement is commercially available under the trade designation "TXI III™" from Texas Industries, Inc. of Midlothian, Texas. When used, the ASTM Type III cement is generally included in the additive in an amount in the range of from about 1 part to about 50 parts by weight.

Yet another component which can be included in the additive is a particulate silica such as fumed silica or ultra-fine silica. The silica functions in a cement slurry to prevent after setting compressive strength retrogression in hot wells. When used, the silica is preferably included in the additive in an amount in the range of from about 0.1 to about 50 parts by weight.

A preferred universal particulate solid additive of this invention for improving the properties of a cement slurry is comprised of iron chloride selected from the group of ferrous

chloride, ferric chloride and mixtures thereof present in an amount of about 10 parts by weight, a dispersing agent comprised of the condensation polymer product of acetone, formaldehyde and sodium sulfite present in an amount of about 13 parts by weight, tartaric acid present in an amount of about 0.4 parts by weight, hydroxyethylcellulose present in an amount of about 2 parts by weight and an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in an amount of about 8 parts by weight.

Additional universal additives of this invention are basically comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight, an alkaline-earth metal halide, preferably chloride, present in an amount in the range of from about 5 to about 60 parts by weight, an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight, and a viscosity increasing hydratable polymer present in an amount in the range of from about 1% to about 50% by weight.

As indicated above, the iron chloride can be ferrous chloride, ferric chloride or mixtures thereof. The iron chloride functions synergistically with the alkali or alkaline-earth metal halide and other components of the additive to overcome the effect of a high metal sulfate concentration in a cement and to shorten the thickening time of a slurry of the

cement to an acceptable range. That is, the iron chloride in combination with the alkali or alkaline-earth metal halide and other components of the additive cause the cement to hydrate in a normal and predictable manner.

A variety of alkali or alkaline-earth metal halides can be utilized in the additive which function synergistically with the iron chloride as described above. Preferred such compounds are calcium chloride, sodium chloride, potassium chloride and ammonium chloride, with calcium chloride being the most preferred.

The organic acid in the additive controls the viscosity of the cement slurry, i.e., it prevents the premature gelation of the slurry and improves the rheology of the slurry over a broad density range. Various organic acids can be utilized in the additive including, but not limited to, tartaric acid, citric acid, gluconic acid, oleic acid, phosphoric acid and uric acid. Of these, tartaric acid is preferred.

A variety of viscosity increasing hydratable polymers can also be utilized in the additive including, but not limited to, carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, vinyl sulfonated polymers, hydratable graft polymers and other hydratable polymers known to those skilled in the art. Of these, hydroxyethylcellulose is preferred. The hydratable polymer utilized adds viscosity to the cement slurry and functions to reduce fluid loss from the slurry.

As indicated above, the additive preferably also includes

a number of other components which provide improved properties to a cement slurry. That is, the additive preferably also includes a defoaming agent such as polydimethylsiloxane present in the additive in an amount in the range of from about 0.01 to about 5 parts by weight, a dispersing agent as described above in an amount in the range of from about 1 to about 20 parts by weight, an ultra-fine particulate hydraulic cement in an amount in the range of from about 1 to about 50 parts by weight, an ASTM Type III cement as described above in an amount in the range of from about 1 part to about 50 parts by weight and fumed or ultra-fine silica in an amount in the range of from about 0.1 to about 50 parts by weight.

Another preferred universal particulate solid additive of this invention for improving the properties of a cement slurry is comprised of iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount of about 10 parts by weight, calcium chloride present in an amount of about 14 parts by weight, tartaric acid present in an amount of about 0.3 parts by weight, hydroxyethylcellulose present in an amount of about 12 parts by weight, a defoaming agent comprised of polydimethylsiloxane present in an amount of about 0.3 parts by weight, a dispersing agent comprised of the condensation polymer product of acetone, formaldehyde and sodium sulfite present in an amount of about 11 parts by weight, an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram

present in an amount of about 8 parts by weight, a particulate ASTM Type III cement present in an amount of about 8 parts by weight and fumed silica present in an amount of about 8 parts by weight.

The additives of this invention can be mixed with a cement slurry using various techniques known to those skilled in the art. A particularly suitable technique is to combine the additive used with the water utilized in a mixer followed by the hydraulic cement used.

The present invention also provides methods of converting the viscosity, thickening time, after setting compressive strength, fluid loss and other properties of a cement slurry comprised of a surface construction grade or better hydraulic cement and water to those properties which are particularly suitable for cementing oil and gas wells. Such methods basically comprise combining a universal particulate solid additive of this invention as described above with the construction grade or better cement slurry in an amount in the range of from about 0.1% to about 30% by weight of the cement in the slurry. As described above, the resulting cement slurry containing the additive has properties particularly suitable for use in cementing oil and gas wells.

Additional methods are provided by the present invention for cementing a subterranean zone penetrated by a well bore. The subterranean zone can have a static temperature of up to about 230°F and the construction grade or better cement slurry utilized can have a density in the range of from about 12 to 17

pounds per gallon. In accordance with the methods, a universal particulate solid additive of this invention is combined with the construction grade or better cement slurry in an amount in the range of from about 0.1% to about 30% by weight of the cement in the slurry. The resulting cement slurry having improved properties is pumped into the subterranean zone to be cemented by way of the well bore penetrating it and the cement slurry is then allowed to set into a hard impermeable mass in the zone.

In order to further illustrate the universal additives and methods of this invention, the following examples are given.

Example 1

A variety of cement slurries having various densities and utilizing various API hydraulic cements, fresh water or salt water and various quantities of a universal additive of this invention were prepared. The slurries were tested for thickening time, fluid loss, rheology (plastic viscosity/yield point), compressive strengths and shear bond strengths at various temperatures. The tests were run in accordance with the procedures set forth in the API Specification For Materials And Testing For Well Cements, API Specification 10, 5th Edition, dated July 1, 1990, of the American Petroleum Institute.

The universal additive utilized in the tests was comprised of 10 parts by weight ferric chloride, 13 parts by weight of a dispersing agent comprised of the condensation polymer product of acetone, formaldehyde and sodium sulfite, 0.4 parts by

weight tartaric acid, 2 parts by weight hydroxyethylcellulose and 8 parts by weight of a particulate ultra-fine hydraulic cement having a maximum particle size of about 15 microns and a specific surface area of about 12,000 square centimeters per gram. The additive was mixed with the cement slurries tested in the amounts indicated in Table I below. In a number of the tests, the cement slurry was tested with and without the additive of this invention. In order of the tests, a conventional set retarding agent was substituted for the universal additive of this invention or included in the cement slurry with the universal additive. Also, fumed silica was included in some of the cement slurries tested.

The results of these tests are given in Table I below.

TABLE I (Page I)

Properties Of Cement Slurries Containing Universal Cement Additive

Test No.	Cement In The Slurry Tested, Country, Manufacturer and API Class	Water In Slurry, % by Weight of Cement	Universal Additive, % by Weight of Cement	Set Retarder, % by Weight of Cement	Fumed Silica, % by Weight of Cement	Slurry Density, Pounds Per Gallon	Thickening Time, Hrs:Min			Fluid Loss at 140•F, cc/30 min	PV/YP		Compressive Strength, psi								
													140•F			180•F			250•F		
							140•F	180•F	250•F		80•F	140•F	Time to 50 psi, hr:min	Time to 500 psi, hr:min	24 hr	Time to 50 psi, hr:min	Time to 50 psi hr:min	24 hr	Time to 50 psi, hr:min	Time to 500 psi, hr:min	24 hr
1	Nigeria Eagle G	44	-	-	-	15.9	0:52	-	-	1907	39/27	54/71	1:21	2:02	3073	-	-	-	-	-	-
2	Nigeria Eagle G	44	1.5	-	-	15.9	1:07	-	-	450	60/8	57/50	1:12	2:40	3185	-	-	-	-	-	-
3	Bolivia Warnes A	46	-	-	-	15.6	0:55	-	-	1950	51/78	-	1:59	3:16	2030	-	-	-	-	-	-
4	Bolivia Warnes A	46	1.5	-	-	15.6	1:21	-	-	477	65/30	48/28	3:22	5:39	2108	-	-	-	-	-	-
5	India Kujang G	44	-	-	-	15.9	1:10	-	-	1900	30/22	57/11	1:40	2:54	2816	-	-	-	-	-	-
6	India Kujang G	44	1.5	-	-	15.9	1:13	-	-	600	44/10	39/16	1:56	2:55	3123	-	-	-	-	-	-
7	Bolivia Warnes A	46	-	0.5[2]	-	15.6	-	2:22	-	-	-	-	-	-	-	6:46	7:57	2079	-	-	-
8	Bolivia Warnes A	46	1.5	0.5[2]	-	15.6	-	6:06	-	-	-	-	-	-	-	19:00	22:44	574	-	-	-
9	India Kujang G	56	-	0.65[3]	35	15.8	-	-	4:28	-	-	-	-	-	-	-	-	-	4:22	5:00	2628
10	India Kujang G	56	1.5	0.65[3]	35	15.8	-	-	2:16	-	-	-	-	-	-	-	-	-	4:31	5:05	2526
11	USA Capital H	48.6	-	0.65[3]	35	16.4	-	-	7:50	-	-	-	-	-	-	-	-	-	16:09	18:43	1481
12	USA Capital H	48.6	1.5	0.65[3]	35	16.4	-	-	2:59	-	-	-	-	-	-	-	-	-	1:25	5:20	2512
13	____ Baturaja A	58.2	-	0.65[3]	35	15.6	-	-	4:44	-	-	-	-	-	-	-	-	-	8:47	10:35	2173
14	____ Baturaja A	58.2	1.5	0.65[3]	35	15.6	-	-	3:17	-	-	-	-	-	-	-	-	-	6:01	6:41	2621
15	____ Baturaja A	53.7	5.18[1]	0.65[3]	35	15.6	-	-	2:56	-	-	-	-	-	-	-	-	-	1:42	4:41	2429
16	USA Capital H	39.1	-	0.5[2]	-	16.4	-	5:50	-	-	-	-	-	-	-	14:03	15:20	1455	-	-	-
17	USA Capital H	39.1	1.5	0.5[2]	-	16.4	-	8:44	-	-	-	-	-	-	-	14:00	18:23	1571	-	-	-
18	India Kujang G	44.8	-	0.5[2]	-	15.8	-	3:23	-	-	-	-	-	-	-	4:51	5:55	2800	-	-	-
19	India Kujang G	44.8	1.5	0.5[2]	-	15.8	-	4:21	-	-	-	-	-	-	-	9:38	11:22	2543	-	-	-

TABLE I (Page 2)

Properties Of Cement Slurries Containing Universal Cement Additive

Test No.	Cement In The Slurry Tested, Country, Manufacturer and API Class	Water In Slurry, % by Weight of Cement	Universal Additive, % by Weight of Cement	Set Retarder, % by Weight of Cement	Fumed Silica, % by Weight of Cement	Slurry Density, Pounds Per Gallon	Thickening Time, Hrs:Min			Fluid Loss at 140°F, cc/30 min	PV/YP		Compressive Strength, psi								
													140°F			180°F			250°F		
							140°F	180°F	250°F		80°F	140°F	Time to 50 psi, hr:min	Time to 500 psi, hr:min	24 hr	Time to 50 psi, hr:min	Time to 50 psi hr:min	24 hr	Time to 50 psi, hr:min	Time to 500 psi, hr:min	24 hr
20	____ Baturaja A	46.3	-	0.5[2]	-	15.6	-	3:38	-	-	-	-	-	-	-	7:37	8:58	2200	-	-	-
21	____ Baturaja A	46.3	1.5	0.5[3]	-	15.6	-	6:12	-	-	-	-	-	-	-	14:10	16:32	1866	-	-	-
22	____ Baturaja A	42.3	5.18[1]	0.5[3]	-	15.6	-	13:20	-	-	-	-	-	-	-	No Set	No Set	No Set	-	-	-
23	____ Baturaja A	42.3	5.18[1]	0.5[3]	-	15.6	-	12:17	-	-	-	-	-	-	-	28:54	38:20	No Set	-	-	-
24	____ Baturaja A	53.7	5.18[1]	0.65[3]	35	15.6	-	-	5:12	-	-	-	-	-	-	-	-	-	7:52	8:53	2514

[1] Additive dissolved in _________ fresh water in an amount of ___% by weight of solution

[2] Set retarder was sodium lignosulfonate

[3] Set retarder was calcium lignosulfonate

From Table I, it can be seen that all of the various slurries tested which contained the additive of this invention had excellent properties and were suitable for oil and gas well cementing applications.

Example 2

A variety of cement slurries having various densities and utilizing various API hydraulic cements, fresh water or salt water and various quantities of another universal additive of this invention were prepared. The slurries were tested for thickening time, fluid loss, rheology (plastic viscosity/yield point), compressive strengths and shear bond strengths at various temperatures. The tests were run in accordance with the procedures set forth in the API Specification For Materials And Testing For Well Cements, API Specification 10, 5th Edition, dated July 1, 1990, of the American Petroleum Institute.

The universal additive utilized in the tests was comprised of 10 parts by weight ferric chloride, 14 parts by weight calcium chloride, 0.3 parts by weight tartaric acid, 12 parts by weight hydroxyethylcellulose, 0.3 parts by weight of a polydimethylsiloxane defoaming agent, 11 parts by weight of a dispersing agent comprised of the condensation product of acetone, formaldehyde and sodium sulfite, 8 parts by weight of a particulate ultra-fine hydraulic cement having a maximum particle size of about 15 microns and a specific surface area of about 12,000 square centimeters per gram, 8 parts by weight of ASTM Type III cement (commercially available, for example

from Texas Industries of Midlothian, Texas) and 8 parts by weight of fumed silica. The additive was mixed with the cement slurries tested in the amounts indicated in Table II below.

The results of these tests are given in Table II below.

TABLE II

Properties Of Cement Slurries Containing Universal Additive

Test No.	Cement In The Slurry Tested, Manufacturer and API Class	Water In Slurry, % by Weight Cement	Universal Additive, % By Weight of Cement	Slurry Density, Pounds Per Gallon	Thickening Time, Hrs:Min 100•F	Thickening Time, Hrs:Min 140•F	Fluid Loss, CC/30 Min 80•F	Fluid Loss, CC/30 Min 140•F	PV/YP 800•F	PV/YP 140•F	24 Hr Compressive Strength, psi 100•F	24 Hr Compressive Strength, psi 140•F	48 Hr Compressive Strength, psi 100•F	48 Hr Compressive Strength, psi 140•F	140•F Shear Bond Strength, psi 48hrs	140•F Shear Bond Strength, psi 7days
1	Capital H	54.53	4	15	-	3:33	0	210	144/39	107/21	770	91	1895	2140	-	-
2	Capital H	100.3	11	12.8	13:12	-	0	64	125/25	117/18	0	0	425	398	-	-
3	Fredonia H	54.53	4	15	-	4:40	0	267	168/31	119/36	949	2810	3020	3720	-	-
4	Fredonia H	100.3	11	12.8	18:00	-	0	91	125/25	102/23	0	88	662	1055	-	-
5	Lone Star H	54.53	4	15	-	4:00	0	240	122/28	116/22	1051	860	2130	1656	193	273
6	Lone Star H	100.3	11	12.8	13:30	-	0	72	107/18	85/15	0	0	709	506	119	178
7	Capital A	59.5	4.5	14.6	-	2:22	0	266	138/47	95/30	2540	3100	3780	4170	-	-
8	Capital A	100.3	11	12.8	6:20	-	0	82	117/28	117/28	554	906	975	1378	-	-
9	Blue Circle A	59.5	4.5	14.6	-	2:55	0	160	131/50	120/68	2000	3250	3810	4490	-	-
10	Blue Circle A	100.3	11	12.8	10:10	-	0	76	113/22	165/35	250	425	856	1050	-	-
11	TX. Lehigh A	59.5	4.5	14.6	-	2:10	0	196	114/21	72/18	2280	3060	2430	2270	336	433
12	TX. Lehigh A	100.3	11	12.8	8:22	-	0	42	129/24	79/16	416	634	770	1086	148	183
13	Lone Star A	59.5	4.5	14.6	-	2:20	0	231	108/44	98/37	1858	3210	3670	4020	-	-
14	Lone Star A	100.3	11	12.8	9:00	-	0	64	156/33	153/30	412	528	924	1206	-	-
15	Ekshaw G	57.25	4.25	14.8	-	2:40	0	194	113/44	111/42	1920	2910	3460	4060	-	-
16	Ekshaw G	100.3	11	12.8	14:00	-	0	68	128/22	128/22	25	13	704	900	-	-
17	Dykerhoff G	57.25	4.25	14.8	-	3:20	0	300	116/18	77/20	2140	2670	3220	3510	-	-
18	Dykerhoff G	100.3	11	12.8	12:59	-	0	80	102/20	81/17	203	11	575	944	-	-
19	Bolivia G#4	57.25	4.25	14.8	-	3:40	0	250	137/21	110/20	1326	2730	3100	4600	-	-
20	Bolivia G#4	100.3	11	12.8	13:50	-	0	44	111/16	90/8	0	0	641	1026	-	-

From Table II it can be seen that all of the various slurries tested had excellent properties and were suitable for oil and gas well cementing applications.

Example 3

The tests described above were repeated utilizing five cement slurries at two different densities with and without the universal additive of this invention. The results of these tests are given in Table III below.

TABLE III

Properties Of Cement Slurries With And Without Universal Additive

Test No.	Cement In The Slurry Tested, Manufacturer and API Class	Water in Slurry, % by Weight Cement	Universal Additive, % by Weight of Cement	Slurry Density, Pounds Per Gallon	Thickening Time, Hrs:Min		140•F Fluid Loss CC/30 Min	PV/YP		24 Hr Compressive Strength, psi		48 Hr Compressive Strength, psi	
					100•F	140•F		80•F	140•F	100•F	140•F	100•F	140•F
1	Capital H	100.3	11	12.8	13:12	-	64	125/25	117/18	0	0	425	398
2	Capital H	54.3	4	15	-	3:33	210	144/39	107/21	770	931	1895	2140
3	TX. Lehigh A	100.3	11	12.8	8:22	-	42	129/24	79/16	416	634	770	1086
4	TX. Lehigh A	59.3	4.5	14.6	-	2:10	196	114/21	72/18	2280	3060	2430	2270
5	Ekshaw G	100.3	11	12.8	14:00	-	68	128/22	128/22	25	13	704	800
6	Ekshaw G	57.25	4.25	14.8	-	2:40	194	113/44	111/42	1920	2910	3460	4060
7	TXI Type I/II[1]	100.3	11	12.8	7:47	-	98	132/28	125/22	332	110	819	1025
8	TXI Type I/II[1]	59.4	4.5	14.6	-	2:03	216	123/32	114/42	1857	2830	2720	3990
9	TOPPA Type I/II[1]	100.3	11	12.8	8:40	-	68	140/28	95/16	547	664	861	991
10	TOPPA Type I/II[1]	59.4	4.5	14.6	-	2:13	216	114/30	68/19	2120	2970	3040	3860
11	Capital H	96.43	0	12.8	24+	-	1905	4.5/1.5	3.75/1.75	Settled by 40%		-	-
12	Capital H	54.5	0	15	-	3:05	1943	14.5/7.5	10.5/14.5	1065	1943	1718	2940
13	TX. Lehigh A	96.43	0	12.8	24+	-	1475	4.5/1.5	4.5/1.5	Settled by 50%		-	-
14	TX. Lehigh A	59.74	0	14.6	-	1:29	1748	13.5/5.5	10.5/7.5	1769	2160	2450	2700
15	Exshaw G	96.43	0	12.8	24+	-	1750	4.5/1.5	3.75/1.75	Settled by 20%		-	-
16	Exshaw G	59.63	0	14.8	-	4:04	1896	16.5/10.5	13.5/16.5	1401	2230	1769	2620
17	TXI Type I/II[1]	96.43	0	12.8	23:45	-	1825	6/2	4.5/2.5	Settled by 30%		-	-
18	TXI Type I/II[1]	59	0	14.6	-	2:10	1710	12/10	17/17	1790	2820	2460	2530
19	TOPPA Type I/II[1]	96.43	0	12.8	22:30	-	1610	6/3	3/5	Settled by 20%		-	-
20	TOPPA Type I/II[1]	59	0	14.6	-	1:45	1585	12/8	14/10	1646	2030	2260	2800

[1] Construction grade cements

From Table III it can be seen that the presence of the universal additive of this invention in the various cement slurries tested significantly improved the properties of the cement slurries.

Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

What is claimed is:

1. A universal additive for improving the properties of a cement slurry to be utilized for cementing a well comprising:

iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight;

an alkali or alkaline-earth metal halide present in an amount in the range of from about 5 to about 60 parts by weight;

an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight; and

a hydratable polymer present in an amount in the range of from about 1 to about 50 parts by weight.

2. The additive of claim 1 wherein said alkali or alkaline-earth metal chloride is selected from the group of calcium chloride, sodium chloride, potassium chloride and ammonium chloride.

3. The additive of claim 1 wherein said organic acid is selected from the group of tartaric acid, citric acid, gluconic acid, oleic acid, phosphoric acid and an uric acid.

4. The additive of claim 1 wherein said hydratable polymer is selected from the group of carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, and vinyl sulfonate polymers.

5. The additive of claim 1 which further comprises a polydimethylsiloxane defoaming agent present in said additive in an amount in the range of from about 0.01 to about 5 parts

by weight.

6. The additive of claim 1 which further comprises a dispersing agent comprised of the condensation polymer product of an aliphatic ketone, an aliphatic aldehyde and a compound which introduces acid groups into the polymer present in said additive in an amount in the range of from about 1 to about 20 parts by weight.

7. The additive of claim 1 which further comprises an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

8. The additive of claim 1 which further comprises a particulate ASTM Type III cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

9. The additive of claim 1 which further comprises particulate silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

10. A universal particulate solid additive for improving the properties of a cement slurry to be utilized for cementing a well comprising:

iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount of about 10 parts by weight;

calcium chloride present in an amount of about 14

parts by weight;

tartaric acid present in an amount of about 0.3 parts by weight;

hydroxyethylcellulose present in an amount of about 12 parts by weight;

polydimethylsiloxane present in an amount of about 0.3 parts by weight;

the condensation polymer product of acetone, formaldehyde and sodium sulfite present in an amount of about 11 parts by weight;

a particulate ultra-fine hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in an amount of about 8 parts by weight;

a particulate ASTM Type III cement present in an amount of about 8 parts by weight; and

fumed silica present in an amount of about 8 parts by weight.

11. A method of converting the properties of a cement slurry comprised of a surface construction grade or better hydraulic cement and water to those properties which are particularly suitable for cementing oil and gas wells which comprises:

combining a universal additive with said cement slurry in an amount in the range of from about 0.1% to about 30% by weight of said hydraulic cement in said slurry, said additive including iron chloride selected from the group of

ferrous chloride, ferric chloride and mixtures thereof, an alkali or alkaline-earth metal halide, an organic acid and a hydratable polymer.

12. The method of claim 11 wherein said iron chloride in said additive is present therein in an amount in the range of from about 0.5 to about 30 parts by weight.

13. The method of claim 11 wherein said alkaline-earth metal halide in said additive is calcium chloride present in an amount in the range of from about 5 to about 60 parts by weight.

14. The method of claim 11 wherein said organic acid in said additive is tartaric acid present in an amount in the range of from about 0.1 to about 10 parts by weight.

15. The method of claim 11 wherein said hydratable polymer in said additive is hydroxyethylcellulose present in an amount in the range of from about 1 to about 10 parts by weight.

16. The method of claim 11 wherein said additive further includes a defoaming agent comprised of polydimethylsiloxane present in said additive in an amount in the range of from about 0.01 to about 5 parts by weight.

17. The method of claim 11 wherein said additive further includes a dispersing agent comprised of the condensation polymer product of an aliphatic ketone, an aliphatic aldehyde and a compound which introduces acid groups into the polymer present in said additive in an amount in the range of from about 1 to about 20 parts by weight.

18. The method of claim 11 wherein said additive further includes an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in said additive in an amount in the range of from about 1 to about 50 by weight.

19. The method of claim 11 wherein said additive further includes an ASTM Type III particulate cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

20. The method of claim 11 wherein said additive further includes particulate silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

21. A method of cementing a subterranean zone penetrated by a well bore at a temperature up to about 230°F utilizing a cement slurry comprised of a surface construction grade or better hydraulic cement and water having a density in the range of from about 12 to about 17 pounds per gallon comprising the steps of:

(a) combining a universal additive with said cement slurry in an amount in the range of from about 0.1% to about 30% by weight of said hydraulic cement in said slurry, said additive including iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof, an alkali or alkaline-earth metal halide, an organic acid and a

hydratable polymer;

(b) pumping the cement slurry containing said additive formed in step (a) into said subterranean zone by way of said well bore; and

(c) allowing said cement slurry to set into a hard impermeable mass in said zone.

22. The method of claim 21 wherein said iron chloride in said additive is present therein in an amount in the range of from about 0.5 to about 30 parts by weight.

23. The method of claim 21 wherein said alkaline-earth metal halide in said additive is calcium chloride present in an amount in the range of from about 5 to about 60 parts by weight.

24. The method of claim 21 wherein said organic acid in said additive is tartaric acid present in an amount in the range of from about 0.01 to about 10 parts by weight.

25. The method of claim 21 wherein said hydratable polymer in said additive is, hydroxyethylcellulose present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

26. The method of claim 21 wherein said additive further includes a defoaming agent comprised of polydimethylsiloxane present in said additive in an amount in the range of from about 0.01 to about 5 parts by weight.

27. The method of claim 21 wherein said additive further includes a dispersing agent comprised of the condensation polymer product of an aliphatic ketone, an aliphatic aldehyde

and a compound which introduces acid groups into the polymer present in said additive in an amount in the range of from about 1 to about 20 parts by weight.

28. The method of claim 21 wherein said additive further includes an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in said additive in an amount in the range of from about 1 to about 50 by weight.

29. The method of claim 21 wherein said additive further includes an ASTM Type III particulate cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

30. The method of claim 21 wherein said additive further includes particulate silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

31. A universal additive for improving the properties of a cement slurry to be utilized for cementing a well comprising:

iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount in the range of from about 0.5 to about 30 parts by weight;

a dispersing agent present in an amount in the range of from about 1 to about 20 parts by weight;

an organic acid present in an amount in the range of from about 0.01 to about 10 parts by weight;

a hydratable polymer present in an amount in the range of from about 1 to about 20 parts by weight; and

an ultra-fine particulate hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in an amount in the range of from about 1 to about 50 parts by weight.

32. The additive of claim 31 wherein said dispersing agent is comprised of the condensation polymer product of an aliphatic ketone, an aliphatic aldehyde and a compound which introduces acid groups into the polymer.

33. The additive of claim 31 wherein said organic acid is selected from the group of tartaric acid, citric acid, gluconic acid, oleic acid, phosphoric acid and an uric acid.

34. The additive of claim 31 wherein said hydratable polymer is selected from the group of carboxymethylcellulose, hydroxyethylcellulose, carboxymethylhydroxyethylcellulose, and

vinyl sulfonate polymers.

35. The additive of claim 31 which further comprises a polydimethylsiloxane defoaming agent present in said additive in an amount in the range of from about 0.01 to about 5 parts by weight.

36. The additive of claim 31 which further comprises an alkali or alkaline-earth metal halide present in said additive in an amount in the range of from about 5 to about 20 parts by weight.

37. The additive of claim 31 which further comprises a particulate ASTM Type III cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

38. The additive of claim 31 which further comprises particulate silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

39. A universal particulate solid additive for improving the properties of a cement slurry to be utilized for cementing a well comprising:

iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof present in an amount of about 10 parts by weight;

the condensation polymer product of acetone, formaldehyde and sodium sulfite present in an amount of about 13 parts by weight;

tartaric acid present in an amount of about 0.4 parts by weight;

hydroxyethylcellulose present in an amount of about 2 parts by weight; and

a particulate ultra-fine hydraulic cement having a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram present in an amount of about 8 parts by weight.

40. The additive of claim 39 which further comprises:

polydimethylsiloxane present in an amount of about 0.3 parts by weight;

calcium chloride present in an amount of about 14 parts by weight;

a particulate ASTM Type III cement present in an amount of about 8 parts by weight; and

fumed silica present in an amount of about 8 parts by weight.

41. A method of converting the properties of a cement slurry comprised of a surface construction grade or better hydraulic cement and water to those properties which are particularly suitable for cementing oil and gas wells which comprises:

combining a universal additive with said cement slurry in an amount in the range of from about 0.1% to about 30% by weight of said hydraulic cement in said slurry, said additive comprising iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof, a dispersing agent, an organic acid, a hydratable polymer and an ultra-fine particulate hydraulic cement.

42. The method of claim 41 wherein said iron chloride in said additive is present therein in an amount in the range of from about 0.5 to about 30 parts by weight.

43. The method of claim 41 wherein said dispersing agent in said additive is the condensation polymer product of acetone, formaldehyde and sodium sulfite and is present in an amount in the range of from about 1 to about 20 parts by weight.

44. The method of claim 41 wherein said organic acid in said additive is tartaric acid present in an amount in the range of from about 0.1 to about 10 parts by weight.

45. The method of claim 41 wherein said hydratable polymer in said additive is hydroxyethylcellulose present in an amount in the range of from about 1 to about 20 parts by weight.

46. The method of claim 41 wherein said ultra-fine particulate hydraulic cement has a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram and is present in said additive in an amount in the range of from about 1 to about 50 by weight.

47. The method of claim 41 wherein said additive further comprises a defoaming agent comprised of polydimethylsiloxane present in said additive in an amount in the range of from about 0.01 to about 5 parts by weight.

48. The method of claim 41 wherein said additive further comprises an alkali or alkaline-earth metal chloride present in said additive in an amount in the range of from about 5 to

about 20 parts by weight.

49. The method of claim 41 wherein said additive further comprises an ASTM Type III particulate cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

50. The method of claim 41 wherein said additive further comprises fumed silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

51. A method of cementing a subterranean zone penetrated by a well bore at a temperature up to about 230°F utilizing a cement slurry comprised of a surface construction grade or better hydraulic cement and water having a density in the range of from about 12 to about 17 pounds per gallon comprising the steps of:

(a) combining a universal additive with said cement slurry in an amount in the range of from about 0.1% to about 30% by weight of said hydraulic cement in said slurry, said additive comprising iron chloride selected from the group of ferrous chloride, ferric chloride and mixtures thereof, a dispersing agent, an organic acid, a hydratable polymer and an ultra-fine particulate hydraulic cement;

(b) pumping the cement slurry containing said additive formed in step (a) into said subterranean zone by way of said well bore; and

(c) allowing said cement slurry to set into a hard impermeable mass in said zone.

52. The method of claim 51 wherein said iron chloride in

said additive is present therein in an amount in the range of from about 0.5 to about 30 parts by weight.

53. The method of claim 51 wherein said dispersing agent in said additive is the condensation polymer product of acetone, formaldehyde and sodium sulfite and is present in an amount in the range of from about 1 to about 20 parts by weight.

54. The method of claim 51 wherein said organic acid in said additive is tartaric acid present in an amount in the range of from about 0.01 to about 10 parts by weight.

55. The method of claim 51 wherein said hydratable polymer in said additive is hydroxyethylcellulose present in said additive in an amount in the range of from about 1 to about 20 parts by weight.

56. The method of claim 51 wherein said ultra-fine particulate hydraulic cement has a maximum particle size of about 15 microns and a specific surface of about 12,000 square centimeters per gram and is present in said additive in an amount in the range of from about 1 to about 50 by weight.

57. The method of claim 51 wherein said additive further includes a defoaming agent comprised of polydimethylsiloxane present in said additive in an amount in the range of from about 0.01 to about 5 parts by weight.

58. The method of claim 51 wherein said additive further includes an alkali or alkaline metal chloride present in said additive in an amount in the range of from about 5 to about 20 parts by weight.

59. The method of claim 51 wherein said additive further includes an ASTM Type III particulate cement present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

60. The method of claim 51 wherein said additive further includes fumed silica present in said additive in an amount in the range of from about 1 to about 50 parts by weight.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00247

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C04B28/02 C04B22/12 E21B33/13 //(C04B28/02,7:02,14:06,
22:12,24:06,24:16,24:38,24:42)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	WO 98 46542 A (HALLIBURTON ENERGY SERVICES INC) 22 October 1998 cited in the application see page 1, line 26 - page 2, line 4; claim 1	1,10,11,21,31,39,41,51
A	US 5 571 318 A (J.E. GRIFFITH ET AL.) 5 November 1996 see column 4, line 19-20 see column 5, line 48-62 see column 6, line 5-30 see column 8, line 7-18	1-60
A	GB 2 156 801 A (SKW TROSTBERG AG) 16 October 1985 see page 1, line 12-15 see page 4, line 25-27; claims 1,2,4	1,3,4,6,31-34

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search	Date of mailing of the international search report
4 May 1999	12/05/1999

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/00247

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